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**(71) Applicant:**

Bayer AG, 5090 Leverkusen, DE

**(72) Inventors:**

Hausmann, Heinz, Dipl.-Chem. Dr.,  
5653 Leichlingen, DE; Voegs, Herbert,  
Dr.; Hanseler, Gerd, Dipl.-Landw. Dr.:  
Scheinpflug, Hans, Dipl.-Biol. Dr.,  
5090 Leverkusen, DE

**(54) Fungicidal agent**

The present invention concerns new combinations with fungicidal action, containing on the one hand a known fungicide and on the other a vegetable oil or a lecithin or linoleic acid.

Patent claims

1. Fungicidal agent, characterized by a content of a combination of active substances consisting of  
(I) one of the following mentioned active substances from the group of fungicides

- a) 1,4-benzoquinone-1-benzoylhydrazono-4-oxime
- b) 6-methyl-2-oxo-1,3-dithiolo(4,5-b)-quinoxaline
- c) N-[2,2,2-trichlor-1-(3,4-dichloraniline)-ethyl]-formamido
- d) N-dichlorofluoromethanesulfonyl-N',N'-dimethyl-N-phenylsulfamide
- e) O-ethyl-S,S-diphenylphosphate
- f) bis-phenyl-(3-trifluoromethyl-phenyl)-1-(1,2,4-triazolyl)-methane
- g) 2-(2-furanyl)-1H-benzimidazole
- h) 1-(4-chlorophenoxy)-3,3-dimethyl-1-(1H-1,2,4-triazol-1-yl)-2-butanone
- i) 8-[(1,1'-biphenyl)-4-yloxy]- $\alpha$ -(1,1-dimethyl-ethyl)-1H-1,2,4-triazol-1-ethanol
- j) 1-(4-chlorophenoxy)-1-(1H-imidazol-1-yl)-3,3-dimethyl-2-butanone
- k) 8-(4-chlorophenoxy)- $\alpha$ -(1,1-dimethylethyl)-1H-1,2,4-triazol-1-ethanol
- l) N-(4-chlorophenyl)-N-cyclopentyl-N'-phenylurea

and a vegetable oil from group II

- a) sesame oil
- b) sunflower oil
- c) olive oil
- d) corn oil
- e) castor oil
- f) cottonseed oil
- g) soybean oil

or

- 2 a) linoleic acid of formula



or

- b) a lecithin.

- 2. Fungicidal agent per Claim 1, characterized in that the weight ratio of a fungicide from group I to a substance from group II in the combinations lies between 1:0.1 and 1:10.
- 3. Fungicidal agent per Claims 1 and 2, characterized in that the weight ratio of a fungicide from group I to a substance from group II in the combinations lies between 1:0.4 and 1:5.5.
- 4. Method for control of fungi, characterized in that one uses a combination of active substances per Claim 1 against fungi or their environment.
- 5. Use of combinations of active substances per Claim 1 to control fungi.
- 6. Method for preparation of fungicidal agents, characterized in that one mixes a combination of active substances per Claim 1 with extenders and/or surfactant agents.

BAYER AKTIENGESELLSCHAFT

5090 Leverkusen, Bayerwerk

Central Division  
Patents, Trademarks and Licenses(stamp:) 17 March 83  
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Type IIIFungicidal agent

The invention concerns new combinations with fungicidal action, containing besides a known fungicide on the one hand, a vegetable oil or a lecithin or linoleic acid on the other hand. The agents according to the invention exhibit greater action than the known fungicidal components.

It is already known that, for example, 1-(4-chlorphenoxy)-3,3-dimethyl-1-(1H-1,2,4-triazol-1-yl)-2-butanone can be used as a fungicide (cf., e.g., R. Wegler, *The Chemistry of Plant Protection and Pest Control Agents*, Vol. 4, page 208, Springer Verlag, Berlin-Heidelberg-New York 1977).

Furthermore, it is known that additions of mineral oils to plant protection formulations can enhance the action of these formulations. Yet these formulations often have drawbacks—for example, an emulsifiable oil can increase the dripping of the spray liquid from the plants, or phytotoxic effects are observed. These and other drawbacks can be hindered by adding lecithin (cf., HU Patent No. 176.051).

It is also known that lecithin can have diversified use, owing to its colloidal, surfactant, emulsifying and physiological properties. Thus, lecithin emulsions are prepared to control pests, such as possess a good stability and adherence (cf. *Ullmann's Encyclopedia of Technical Chemistry*, Vol. 11, pages 549-550, 1960).

Furthermore, insecticidal compositions of adjuvant substances are known, containing, besides an insecticide, a vegetable oil, a vegetable powder, and surfactant adjuvants (cf. Patent application laid open 2 730 205).

Furthermore, it is known that the effectiveness of plant protection agents, such as fungicides or growth regulators, can be enhanced by adding a surfactant substance in concentrations higher than the quantities needed to lower the surface tension (cf. GB 2 057 265). Lecithin also falls among these surfactant substances.

Surprisingly, it has now been found that the new combinations consisting of a known fungicide from group I, for which the following active substances can be mentioned as examples:

- I. a) 1,4-benzoquinone-1-benzoylhydrazone-4-oxime
- b) 6-methyl-2-oxo-1,3-dithiolan(4,5-b)-quinoxaline
- c) N-[2,2,2-trichlor-1-(3,4-dichloraniline)-ethyl]-formamide
- d) N-dichlorfluormethanesulfenyl-N',N'-dimethyl-N-phenylsulfamide
- e) O-ethyl-S,S-diphenylphosphate
- f) bis-phenyl-(3-trifluormethyl-phenyl)-1-(1,2,4-triazolyl)-methane
- g) 2-(2-furanyl)-1H-benzimidazole
- h) 1-(4-chlorphenoxy)-3,3-dimethyl-1-(1H-1,2,4-triazol-1-yl)-2-butanone
- i) 3-[(1,1'-biphenyl)-4-yloxy]- $\alpha$ -(1,1-dimethyl-ethyl)-1H-1,2,4-triazol-1-ethanol
- j) 1-(4-chlorphenoxy)-1-(1H-imidazol-1-yl)-3,3-dimethyl-2-butanone
- k) 3-(4-chlorphenoxy)- $\alpha$ -(1,1-dimethylethyl)-1H-1,2,4-triazol-1-ethanol
- l) N-(4-chlorbenzyl)-N-cyclopentyl-N'-phenylurea

and

a vegetable oil from group II, for which one can mention as examples:

- II. 1. a) sesame oil  
b) sunflower oil  
c) olive oil  
d) corn oil  
e) castor oil  
f) cottonseed oil  
g) soybean oil

or

- II. 2. a) linolic acid of formula



or

2. b) a lecithin

possess an especially broad fungicidal activity.

Especially preferred are the compounds from group I under b), b) and i) and from group II 1a), 1b), 2a) and 2b).

One may consider it surprising that the combinations of the invention exhibit an enhanced action which goes far beyond the action of conventional fungicidal formulations, wherein the vegetable oils and their components have no effect on their own in the concentrations used for the application. This enhanced action of plant protection agents by adding known, yet ineffective compounds, is especially important, since this reduces the concentration of active substance for the same good results and thus lowers the strain on the environment. Furthermore, one should stress the easy handling of such combinations, which can be used as a tank mixture, i.e., the fungicide is suspended in water at the place of use and the vegetable oil or its individual component, possibly combined with an emulsifying agent, is added. The mixture can be applied directly, so that there are no problems with stability, which is a further advantage. On the other hand, the active substance and vegetable oils or their individual components can also be processed into ready-made formulations in familiar manner.

Thus, the new fungicide combinations are a valuable addition to the field of fungus control.

Fungicidal agents in plant protection are used to control plasmodiophoromycetes, oomycetes, chytridiomycetes, zygomycetes, ascomycetes, basidiomycetes, deuteromycetes.

The good plant toleration of the substances or combinations of substances in the concentrations necessary for control of plant diseases allows a treatment of above-ground plant parts, plantings, seeds, and soil.

As plant protection agents, the combinations of active substances according to the invention can also be used to control the pathogen of wheat brown rust and bean rust.

The enhanced activity effect of the combinations of the invention is especially pronounced with certain concentration ratios. However, the weight ratios of the components in the combinations can be varied in relatively broad ranges. In general, for one part by weight of fungicide of group I

there is 0.1 to 10 parts by weight of one of the substances from group II, preferably 0.4-5.5 parts by weight of a substance from group II.

The active substances or combinations of active substance can be mediated in conventional formulations, such as solutions, emulsions, suspensions, powders, foams, pastes, granulates, aerosols, natural and synthetic fabrics impregnated with active substance, microencapsulations in polymer substances and coated materials for seeds, as well as formulations with combustion units, such as smoke canisters, cans, spirals, etc., as well as ULV cold and warm fog formulations.

These formulations are made in known manner, e.g., by mixing the active substances with extenders, such as liquid solvents, pressurized liquefied gases and/or solid vehicles, possibly making use of surfactant agents, such as emulsifiers and/or dispersing agents and/or foam-generating agents. In the event that water is used as the extender, it is also possible to employ, for example, organic solvents as auxiliary solvents. Basically, the following liquid solvents can be considered: aromatic substances like xylene, toluene, or alkyl-naphthalenes, chlorinated aromatic or chlorinated aliphatic hydrocarbons, such as chlorobenzenes, chloroethylenes or methylene chloride, aliphatic hydrocarbons, such as cyclohexane or paraffins, such as petroleum fractions, alcohols, like butanol or glycol, as well as their ethers and esters, ketones, such as acetone, methylethylketone, methylisobutylketone or cyclohexanone, strongly polar solvents, such as dimethylformamide and dimethylsulfoxide, as well as water; by liquefied gaseous extenders or vehicles is meant such liquids as are in the gas state at normal temperature and under normal pressure, such as aerosol propellant gas, like halogenated hydrocarbons, as well as butane, propane, nitrogen and carbon dioxide; possible solid vehicles are:

for example, natural stone powder, such as kaolin, clay, talc, chalk, quartz, attapulgit, montmorillonite, or diatomaceous earth and synthetic stone powder, such as highly dispersed silicic acid, aluminum oxide and silicates; possible solid vehicles for granulates include: for example, broken and fractionated natural stone such as calcite, marble, mica, sepiolite, dolomite, as well as synthetic granulates made from inorganic and organic flour, as well as granulates from organic material such as sawdust, coconut shells, corn husks and tobacco stems; possible emulsifying and/or foam-generating agents are: for example, non-ionogenic and anionic emulsifiers, like polyoxyethylene/fatty acid esters, polyoxyethylene/fatty alcohol ethers, e.g., alkylaryl polyglycol ether, alkyl sulfonates, alkyl sulfates, aryl sulfonates, as well as protein hydrolysates; possible dispersing agents are: e.g., lignin-sulfite spent liquors and methyl cellulose.

In the formulations, one can use adhesive agents such as carboxymethylcellulose, natural and synthetic powdered, granular, or latex-like polymers, such as gum arabic, polyvinyl alcohol, polyvinyl acetate.

One can use colorants such as inorganic pigments, e.g., iron oxide, titanium dioxide, ferrocyan blue and organic colorants like alizarin, azo- and metal phthalocyanine dyes and trace nutrients such as salts of iron, manganese, boron, copper, cobalt, molybdenum and zinc.

The formulations generally contain between 0.1 and 95 percent by weight of combination of active substance, preferably between 0.5 and 90%.

The combinations according to the invention can be applied in the form of ready formulations. Yet the components contained in the combinations can also be mixed as individual formulations during application, i.e., they can be used in the form of tank mixtures. For better emulsifiability, a conventionally used emulsifier is preferably added to the component from group II up to approximately 10% of the weight fraction of component II.

The combinations of active substance according to the invention can be present in the formulations or in the various forms of application in mixture with other known active substances, such as fungicides, bactericides, insecticides, acaricides, nematocides, herbicides, substances protecting against consumption by birds, growth factors, plant nutrients and soil structure improvers.

The active substances can be used as such, in the form of their formulations or the application forms prepared from them by further dilution, such as ready-to-use solutions, emulsions, suspensions, powders, pastes and granulates. The application is done in normal fashion, e.g., by pouring, dipping, spraying, squirting, nebulizing, evaporating, injecting, slurring, painting, dusting, scattering, dry pickling, moist pickling, wet pickling, slurry pickling, or encrustation.

The concentrations of active substance in the application forms can vary in a rather large range when treating the plant parts. They generally lie between 1 and 0.0001 wt. %, preferably between 0.5 and 0.001%.

When treating seeds, one will generally require active substance quantities of 0.001 to 50 g per kilogram of seeds, preferably 0.01 to 10 g.

When treating soil, concentrations of active substance of 0.00001 to 0.1 wt. %, preferably from 0.0001 to 0.02%, are required at the place of action.

The good fungicidal action of the new combinations is demonstrated by the following examples. While the individual components exhibit weaknesses in their fungicidal action, the combinations display a broad fungicidal action.

#### Example 1

**Puccinia Tenu (Wheat) / protective**

**Solvent:** 0.001% xylene

**Emulsifier:** 0.001% Ca-ABS-n-dodecylbenzene sulfonate

To prepare an effective quantity of active substance, one first emulsifies the oil in elevated amounts of emulsifier and solvent. The desired concentrations are obtained by subsequently adding an appropriate excess concentration of solution of active substance.

To test for protective activity, young plants are inoculated with a spore suspension of *Puccinia recondita* in a 0.1% aqueous agar solution. After drying, the plants are sprayed with the preparation of active substance until dew-moist. The plants remain 24 hours at 20°C and 100% relative humidity in an incubation booth.

The plants are placed in a greenhouse at a temperature of around 20°C and relative humidity of around 80% in order to foster the development of rust pustules.

Table A

## Puccinia Test / protective

Active substance or combination of active substances	Concentration of active substance in ppm	Percent affected by disease
1-(4-chlorophenoxy)-3,3-dimethyl-1- (1H-1,2,4-triazol-1-yl)-2-butanone (Ih) (known)	125	85
sesame oil (II/1a) (known)	60	100 (% attacked)
	120	100
sunflower oil (II/1b) (known)	60	100
	120	100
lecithin (II/2b) (known)	60	100
	120	100
<u>according to the invention</u>		
(Ih) + (II/1a)	125 + 60	50
	125 + 120	50
(Ih) + (II/1b)	125 + 60	70
	125 + 120	50
(Ih) + (II/2b)	125 + 60	85
	125 + 120	50



**Example B**

**Uromyces Test (Beans) / protective**

Solvent: 0.001 % xylene  
Emulsifier: 0.001 % Ca-ABS-n-dodecylbenzene sulfonate

To prepare an effective quantity of active substance, one first emulsifies the oil in elevated amounts of emulsifier and solvent. The desired concentrations are obtained by subsequently adding an appropriate excess concentration of solution of active substance.

To test for protective activity, the young plants are sprayed with the preparation of active substance until drip-wet. After the drying of the spray coating, the plants are inoculated with an aqueous uredospore suspension of the bean rust pathogen (*Uromyces appendiculatus*) and remain one day in a dark moist room at 20 to 22°C and 100% relative humidity.

The plants are then placed in a greenhouse under intense light for 9 days at 20 to 22°C and relative humidity of 70 to 80%.

Evaluation is done 10 days after inoculation.

The compounds according to the following preparation samples exhibit a definite superiority of activity over the state of the art in this test:

Table B

## Uromyces Test / protective

Active substance or combination of active substances	Concentration of active substance in ppm	Percent affected by disease
1-(4-chlorophenoxy)-3,3-dimethyl-1- (1H-1,2,4-triazol-1-yl)-2-butanone (Ih) (known)	125	50
sesame oil (II/1a) (known)	40	0
	80	0
sunflower oil (II/1b) (known)	40	0
	80	0
lecithin (II/2b) (known)	40	0
	80	0
linoleic acid (II/2a) (known)	40	0
	80	0
<u>according to the invention</u>		
(Ih) + (II/2a)	125 + 40	10
	125 + 80	15
(Ih) + (II/1b)	125 + 40	10
	125 + 80	10
(Ih) + (II/2b)	125 + 40	50
	125 + 80	30
(Ih) + (II/1a)	125 + 40	50
	125 + 80	20

100% attacked